Gas and Vapor Induced Coal Swelling

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Abstract

Dilatometric studies have been carried out on coal samples exposed to carbon dioxide at 5, 10 and 15 atmospheres and helium saturated with acetone vapor. Coals investigated included KCER 7463 (65.8%C), KCER 7122 (78.3%C) and KCER 7259 (83.8%C). Coal sample dimensions increased on exposure to both types of environment. Carbon dioxide induced swelling increased as the pressure increased. The swelling magnitude increased as the carbon content decreased, indicating that the macromolecular crosslink density in coal increases with increasing carbon content. The time to reach equilibrium swelling was shorter at higher CO_2 pressures. The swelling effect produced by acetone vapor was generally greater than that produced by CO_2 at 15 atmospheres. In the case of KCER 7259, the effect was reversed. It was estimated that the swelling effect can account for 20 to 50% of the surface area determined by CO_2 BET adsorption methods.

Introduction

Studies on the adsorption of organic vapors by coal (1) and the effect of CO_2 on coal swelling (2) have been carried out recently in order to clarify the role of adsorbate induced swelling in influencing coal surface areas determined by gas adsorption methods. BET surface areas determined by CO_2 adsorption are generally higher than N_2 surface areas (3-6). Dilatometric studies on coal samples exposed to CO_2 at 1 atmosphere showed that volume increases of up to 1.31% could be observed (2). It was concluded that swelling of this type could account for up to 14.5% of the CO_2 surface area.

The dilatometric results at 1 atmosphere indicated, however, that equilibrium swelling had not been reached at these CO_2 pressures, even at exposure times in excess of 240 hours. In the present investigation, the dilatometric studies have been extended to higher CO_2 pressures and studies have also been carried out on coals exposed to acetone vapor. The objective has been to evaluate the effect of gas pressure on the swelling behavior of typical coals, obtain a better estimate of the equilibrium parameters and compare the swelling effect of CO_2 with that of a typical organic vapor whose solubility parameter (7) is closer to that of coal (1).

Experimental

The dilatometer system and the experimental procedures have been described in previous publications. (2,8) The coals investigated included KCER 7259 (sample 1, 83.8%C), KCER 7122 (sample 2, 78.3%C) and KCER 7463 (sample 3, 65.8%C). The coal samples have been described previously in more detail (2). Samples were exposed to helium saturated with acetone vapor (at room temperature) in the acetone exposure experiments.

Results and Discussion

Acetone generally produced a greater swelling effect than CO_2. The KCER 7259 sample was an exception, however, in that CO_2 produced the greater swelling response. The swelling response of the coals to acetone vapor and CO_2 at several pressures is illustrated in Figures 1 to 3. Figure 4 compares the effect of acetone on these coals. In general the order of swelling was : KCER 7259 (sample 1) < KCER 7122 (sample 2) < KCER 7463 (sample 3). At constant pressure the response increased in magnitude as the carbon content decreased, in agreement with

previous results (2). The solubility parameter of acetone (δ = 9.6 cal$^{0.5}$cm$^{-1.5}$) is generally closer to that of coal (1) than the CO_2 value (δ = 6.2 cal$^{0.5}$cm$^{-1.5}$). Thus a greater swelling effect is expected with acetone. The results on KCER 7259 are, however, anomalous and not explained by these considerations. Table 1 summarizes the swelling response of the coal samples after 200 hours of exposure to acetone vapor.

Table 1   Comparison of Swelling Rsponse of Coals after 200 hrs. of
           exposure to Acetone vapor

| Sample | % C | Dimension Change | |
		Specimen 1 microns	Specimen 2 microns
1	83.8	11.4	11.5
2	78.3	219.4	192.3
3	65.8	256.2	209.2

CO_2 induced swelling was investigated by exposing the coal samples to CO_2 at pressures of 5, 10 and 15 atmospheres. The results showed a dependence on the carbon content and pressure. The results are shown in Figures 1 to 3. The response increased with increase in CO_2 pressure but the ultimate response was still generally lower than the values obtained from swelling due to Acetone. This may be seen in two of the three samples. The response due to the highest pressure of CO_2 was greater than that obtained with Acetone vapor in the case of Sample 1. This result may possibly be due to CO_2 molecules creating new pores as the coal swells or the higher pressure of the gas may be modifying the crosslink structure in the coal. A more detailed discussion of the CO_2-induced swelling results is presented elsewhere (9).
    It is of interest to estimate the effect that this measured swelling (volume increase) may have on typical surface area values that have been reported for coals of these carbon contents. To facilitate this assessment it can be assumed initially that all the adsorbed molecules which are contained in the 'monolayer' are contributing volume to a swollen adsorbent-adsorbate system. Surface area values reported in the literature for coals of the same carbon content were employed. (5). The estimated swelling volume increases obtained in this way are compared with the measured volume increases in Tables 2-4.
    The results in Table 2 indicate that the measured swelling may account for 13.8 to 24% of the reported surface area values. At higher pressures the swelling effect may account for higher fractions of the reported surface area values (Tables 3 and 4). It should be noted, however, that adsorption experiments to determine surface area are usually carried out at low pressures with an 'equilibrium' time of approximately 30 minutes whereas the swelling volumes were measured after more prolonged contact times. The estimated contributions of swelling to surface area at high pressures are thus more uncertain. There is also some uncertainty because the surface areas reported in the literature may not exactly represent the coal samples employed in the present study. In addition, because there is an inherent pore structure in coal, pore filling undoubtedly accounts for a large fraction of the adsorption and not all adsorbate contributes to swelling. The results indicate, however, that in low carbon content coals, the swelling of coal by CO_2 may account for a significant fraction of the measured BET surface area.

Table 2   Estimated contribution of swelling to CO_2 surface area
          (pressure = 5 atm).

Sample	% C	CO_2 surface area (m^2g^{-1})	Estimated[b] swelling vol (%)	Measured[a] swelling vol (%)
1	83.8	150	5.4	0.75(13.8)
2	78.3	150	5.4	1.24(22.9)
3	65.8	250	9.0	2.16(24.0)

[a] Expressed as a percentage of estimated swelling in parenthesis
[b] Estimated assuming that all the adsorbed molecules which are contained in the 'monolayer' are contributing volume to a swollen adsorbent – adsorbate system.

Table 3   Estimated contribution of swelling to CO_2 surface area
          (pressure = 10 atm)

Sample	% C	CO_2 surface area (m^2g^{-1})	Estimated[b] swelling vol (%)	Measured[a] swelling vol (%)
1	83.8	150	5.4	0.85(15.6)
2	78.3	150	5.4	2.23(41.3)
3	65.8	250	9.0	3.00(33.2)

[a] Expressed as a percentage of estimated swelling in parenthesis
[b] Estimated assuming that all the adsorbed molecules which are contained in the 'monolayer' are contributing volume to a swollen adsorbent– adsorbate system.

Table 4   Estimated contribution of swelling to CO_2 surface area
          (pressure = 15 atm)

Sample	% C	CO_2 surface area (m^2g^{-1})	Estimated[b] swelling vol (%)	Measured[a] swelling vol (%)
1	83.8	150	5.4	1.33(24.5)
2	78.3	150	5.4	3.11(57.6)
3	65.8	250	9.0	4.18(46.5)

[a] Expressed as a percentage of estimated swelling in parenthesis
[b] Estimated assuming that all the adsorbed molecules which are contained in the 'monolayer' are contributing volume to swollen adsorbent – adsorbate system.

The higher surface areas measured by carbon dioxide adsorption can also result from carbon dioxide dissolving in the coal, during the swelling process, and reaching inner pores which are inaccessible to nitrogen. By this process, the carbon dioxide has solution pathways through the coal to the inner pores that nitrogen cannot reach.

Summary and Conclusions

Significant swelling or volume increases ranging from 0.75 to 4.18% were observed in a range of coal samples when they were exposed to carbon dioxide at pressures up to 15 atmospheres. Increase in pressure produced an increase in swelling response and a decrease in the time required to reach maximum response. A lower carbon content correlates with a higher degree of swelling. The order of swelling was sample 1 ($\%C = 83.8$) < sample 2 ($\%C = 78.3$) < sample 3 ($\%C = 65.8$).

Significant swelling response was observed when the samples were exposed to Acetone vapor. The values of the final swelling response were higher than the equilibrium response obtained by CO_2 swelling at 15 atm for samples 2 and 3. This is probably due to the fact that the solubility parameter of the coals is closer to that of the acetone vapor. The order of swelling was sample 1 < sample 2 < sample 3. A lower carbon content corresponded to a higher degree of swelling. Sample 1 showed anomalous behavior. The exposure to higher pressures of CO_2 produced a higher swelling response in comparison to the Acetone swelling. This could not be conclusively explained and further studies are required to understand the behavior.

CO_2-induced swelling may account for up to 50% of the reported CO_2 surface area values in lignite and subbituminous coals. In bituminous coals, swelling may account for about 20% of the surface area values. Thus, previously reported surface area values of these coals determined by CO_2 adsorption may be overestimated by 20 to 50%, depending on the coal.

References
1. P. J. Reucroft and K. B. Patel, Fuel, 62, 279 (1983).
2. P. J. Reucroft and H. Patel, Fuel, 65, 816 (1986).
3. O. P. Mahajan, Powder Technology, 40, 1 (1984).
4. O. P. Mahajan, "Coal Porosity", in "Coal Structure", edited by R. A. Meyers, p. 51, Academic Press, New York, 1982.
5. O. P. Mahajan and P. L. Walker, Jr., "Porosity of Coal and Coal Products", in Analytical Methods for Coal and Coal Products", Vol. 1, edited by C. Karr, Jr., p. 125, Academic Press, New York, 1978.
6. O. P. Mahajan, "Adsorption and Pore Structure and Coal-Water Interactions", in "Sample Selection, Aging and Reactivity of Coal", edited by R. Klein and R. Wellek, John Wiley and Sons, New York, in press.
7. A. F. M. Barton, "Handbook of Solubility Parameters and Other Cohesion Parameters", CRC Press, Inc., 1983.
8. A. A. Sagues, Rev. Sci. Instrum., 50, 48 (1979).
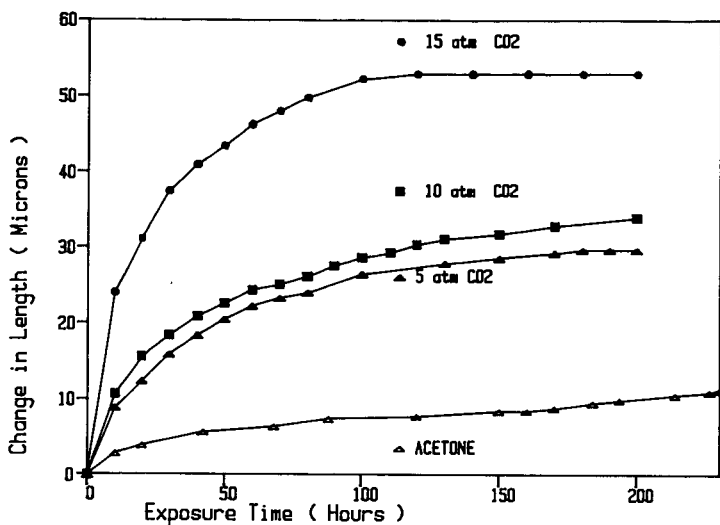9. P. J. Reucroft and A. R. Sethuraman, Energy and Fuels, in press.

Fig. 1. Swelling response of KCER7259 samples on exposure to
acetone vapor and varying pressures of CO_2.

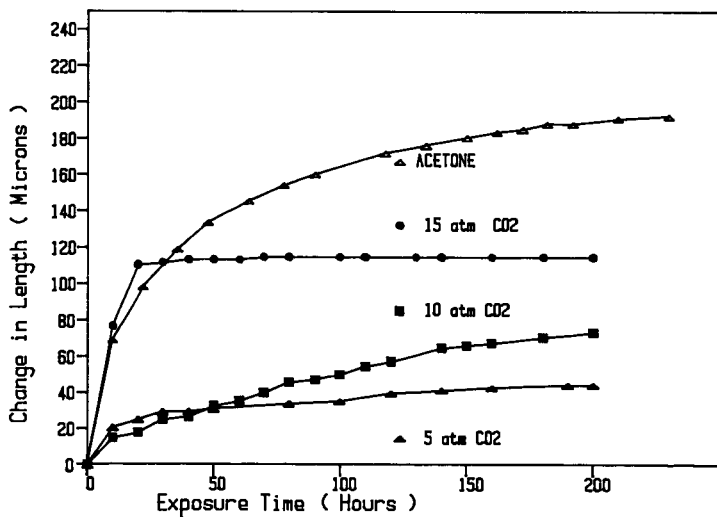Fig. 2. Swelling response of KCER 7122 samples on exposure to
acetone vapor and varying pressures of CO_2.

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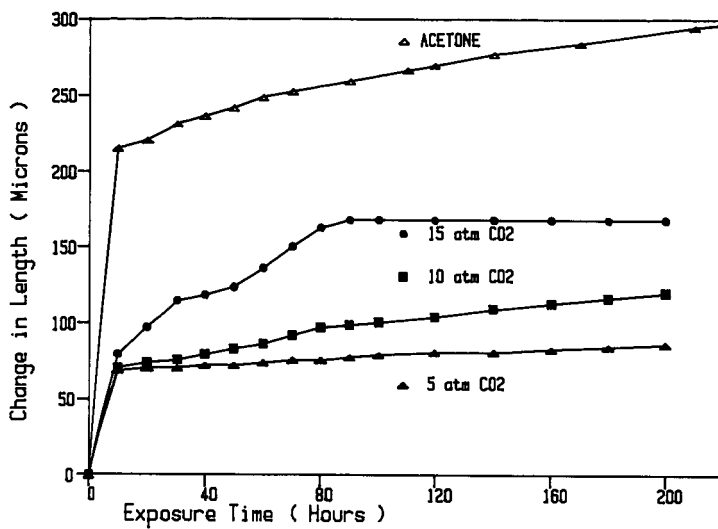Fig. 3. Swelling response of KCER 7463 samples on exposure to
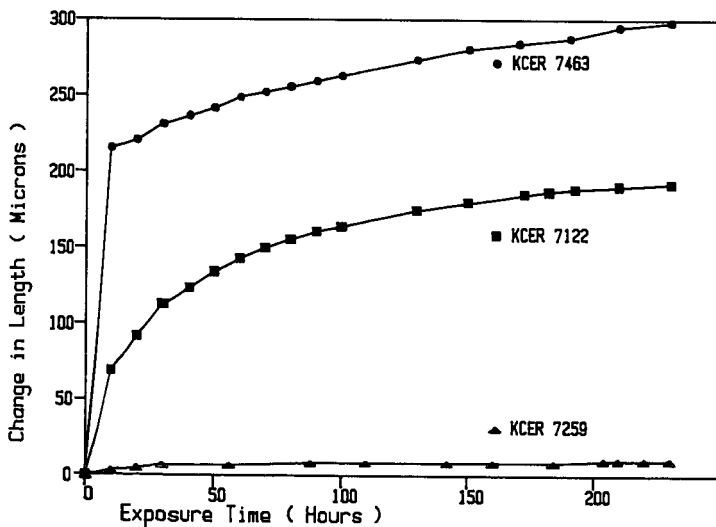acetone vapor and varying pressures of CO_2.

Fig. 4. Swelling response of three coal samples on exposure to
acetone vapor.

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